

JC10 Rec'd PCT/PTO 20 FEB 2002

Customized FORM PTO-1390		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY DOCKET NO P07531US00/BAS
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO 10/049900
INTERNATIONAL APPLICATION NO PCT/AU00/00993	INTERNATIONAL FILING DATE 21 AUGUST 2000	PRIORITY DATE CLAIMED 20 AUGUST 1999		
TITLE OF INVENTION HYDROPHOBIC MATERIAL				
APPLICANT(S) FOR DO/EO/US: JONES, Ashley W. et al.				
Applicant herewith submits to the US Designated/Elected Office (DO/EO/US) the following items and other information				
<input checked="" type="checkbox"/> 1. This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> 2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 USC 371. <input checked="" type="checkbox"/> 3. This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 USC 371(b) and PCT Art. 22 and 39(1). <input checked="" type="checkbox"/> 4. A proper Demand for International Preliminary Examination was made by the 19 th month from the earliest claimed priority date. <input checked="" type="checkbox"/> 5. A copy of the International Application as filed (35 U.S.C. 371 (c)(2)) <input type="checkbox"/> a. is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> b. has been transmitted by the International Bureau. <input type="checkbox"/> c. is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> 6. A translation of the International Application into English (35 U.S.C. 371(c)(2)) <input checked="" type="checkbox"/> 7. Amendments to the claims of the International Appln. under PCT Article 19 (35 USC 371 (c)(3)) <input type="checkbox"/> a. are transmitted herewith (required only if not transmitted by the International Bureau) <input type="checkbox"/> b. have been transmitted by the International Bureau. <input type="checkbox"/> c. have not been made; however, the time limit for making such amendments had NOT expired <input checked="" type="checkbox"/> d. have not been made and will not be made. <input type="checkbox"/> 8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> 9. An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> 10. A translation of the annexes to the Int'l Prelim. Exam. Report under PCT Article 36 (35 U.S.C. 371(c)(5)). Items 11. to 20. below concern document(s) or information included: <input type="checkbox"/> 11. An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98. <input type="checkbox"/> 12. An Assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> 13. A First preliminary amendment . <input type="checkbox"/> 14. A Second or Subsequent preliminary amendment. <input type="checkbox"/> 15. A substitute specification. <input type="checkbox"/> 16. A change of power of attorney and/or address letter. <input type="checkbox"/> 17. A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 & 35 USC 1.821-825 <input type="checkbox"/> 18. A second copy of the published international application under 35 USC 154(d)(4). <input type="checkbox"/> 19. A second copy of the English translation of the international application under 35 USC 154(d)(4). <input type="checkbox"/> 20. Other items or information: <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> A copy of the Notification of Missing Requirements under 35 U.S.C. 371. <input type="checkbox"/> In the event that a petition for extension of time is required to be submitted herewith, and in the event that a separate petition does not accompany this response, applicant hereby petitions under 37 CFR 1.136(a) for an extension of time of as many months as are required to render this submission timely. Any fee is authorized in 17(c)				
Date: 20 Feb 2002				

JC10 Rec'd PCT/PTO 20 FEB 2002

U S APPLICATION NO. <i>(if known)</i> 10/049900		INTERNATIONAL APPLICATION NO. PCT/AU00/00993		ATTORNEY DOCKET NO P07531US00/BAS	
<input checked="" type="checkbox"/> 21. The following fees are submitted: <input checked="" type="checkbox"/> Basic National Fee (37 CFR 1.492 (a) (1)-(5):				CALCULATIONS <i>PTO USL ONLY</i>	
<input checked="" type="checkbox"/> Neither Int'l Prelim. Exam. fee nor Int'l Search fee paid to USPTO \$1040 <input type="checkbox"/> Search Report has been prepared by the EPO or JPO \$ 890 <input type="checkbox"/> No Int'l Prelim Ex. fee paid to USPTO but Int'l Search fee paid to USPTO \$ 740 <input type="checkbox"/> International preliminary examination fee paid to USPTO \$ 710 <input type="checkbox"/> Int'l Prelim. Ex. fee paid to USPTO & all claims satisfied PCT Art. 33(1)-(4) \$ 100					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 1040	
<input type="checkbox"/> Surcharge of \$130 for furnishing the oath or declaration later than from the earliest claimed priority date (37 CFR 1.492(e)).				<input type="checkbox"/> 20 mos. <input type="checkbox"/> 30 mos. +	
CLAIMS		NUMBER FILED	NUMBER EXTRA	RATE	
Total Claims		40 - 20 =	20	X \$18 =	\$ 360
Independent Claims		01 - 03 =		X \$84 =	\$
<input type="checkbox"/> Multiple Dependent Claim(s) (if applicable)				+ \$280 =	\$
TOTAL OF ABOVE CALCULATIONS =				\$ 1400	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				- \$ 700	
SUBTOTAL =				\$ 700	
<input type="checkbox"/> Processing fee of \$130 for furnishing the English translation later than from the earliest claimed priority date (37 CFR 1.492(f)).				<input type="checkbox"/> 20 mos <input type="checkbox"/> 30 mos +	
TOTAL NATIONAL FEE =				\$ 700	
<input type="checkbox"/> Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40 per property				+ \$	
TOTAL FEES ENCLOSED =				\$ 700	
Amount to be				Refunded	\$
				Charged	\$
<input checked="" type="checkbox"/> a. A check in the amount of \$ 700 to cover the above fees is enclosed. <input type="checkbox"/> b. Please charge my Deposit Account No. 12-0555 in the amount of \$ to cover the above fees <input checked="" type="checkbox"/> c. The Commissioner is hereby authorized to charge any additional fees required or credit overpayment to Deposit Account No. 12-0555.					
<i>Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status</i>					
SEND ALL CORRESPONDENCE TO:			SIGNATURE: <i>Douglas E. Jackson</i>		
B. Aaron Schulman			NAME: Douglas E. Jackson		
At the address (below) of CUSTOMER NO. 00881.			REG. NO.: 28518		
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent

In re patent application of: JONES et al.

Serial No.: Unassigned

Examiner: Unassigned

Filed: On even date herewith

Art Unit: Unassigned

For: HYDROPHOBIC MATERIAL

Dckt No.: P07531US00/BAS

PRELIMINARY AMENDMENT

Commissioner of Patents

Washington, D.C. 20231

SIR:

Prior to examination, please amend the above-identified application as follows:

IN THE CLAIMS

Cancel claims 41 and 42.


A clean version of all pending claims is provided herewith in **Attachment A**. It will be noted that claims 3-5, 9-14, 16-19, 21, 23-28, 32-34 and 36-40 have been amended relative to the previously provided version as shown by the marked up version thereof in **Attachment B** provided herewith; and that new claims 11-17 have been added.

REMARKS

The present amendment is made to eliminate multiple dependent claims (the new claims continue some the multiple dependent subject matter), and thus eliminate the requirement for a multiple claim fee.

Respectfully submitted,

Date: 2/20/02


By: Douglas E. Jackson
Registration No.: 28,518

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ATTACHMENT AClean Replacement/New Claims (entire set of pending claims)

Following herewith is a clean copy of the entire set of pending claims.

1. A method of forming a material capable of being applied to a surface, the method including the steps of:
 - (a) providing precursors capable of reacting to form a gel,
 - (b) reacting the precursors together to form the gel;
 - (c) adding a particulate material to the gel to form a mixture, the particulate material being capable of chemically bonding with the gel; and
 - (d) treating the mixture such that a modified gel is formed in which the particulate material is bound to the gel, and the modified gel is capable of forming a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water has a contact angle on the surface of at least 150°.
2. The method according to claim 1 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 155°.
3. (amended) The method according to claim 1 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 160°.
4. (amended) The method according to claim 1 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 165°.
5. (amended) The method according to claim 1 wherein the precursors provided in step (a) include at least water, a solvent, and a metal alkoxide.
6. The method according to claim 5 wherein the solvent comprises an alcohol.

7. The method according to claim 6 wherein the alcohol is selected from the following group: methanol; ethanol; isopropanol; and butanol.
8. The method according to claim 5 wherein the solvent is selected from a group comprising: hexane; and diethyl ether.
9. (amended) The method according to claim 5 wherein the metal alkoxide is selected from the following group: tetramethoxysilane; tetraethoxysilane; titanium tetraisopropoxide; titanium tetrameahoxide; titanium tetraethoxide; titanium tetrabutoxide; and zirconium n-butoxide.
10. (amended) The method according to claim 1 wherein step (b) of reacting the precursors together comprises refluxing the precursors for an extended period.
11. (amended) The method according to claim 1 wherein the particulate material comprises particles having substantially equal diameters.
12. (amended) The method according to claim 1 wherein the particulate material comprises particles having a spectrum of diameters.
13. (amended) The method according to claim 11 wherein at least some of the particles have diameters within a range from 1 nanometer to 1 micrometer.
14. (amended) The method according to claim 11 wherein at least some of the particles have diameters within a range from 1 nanometer to 100 nanometers.
15. The method according to claim 11 wherein substantially all particles have diameters within a range from 1 nanometer to 500 micrometers.
16. (amended) The method according to claim 11 wherein the particles have a primary particle diameter in a range from 5 nanometers to 50 nanometers.

17. (amended) The method according to claim 11 wherein the particles have an average particle size in a range from 5 nanometers to 20 nanometers.
18. (amended) The method according to claim 11 wherein the average particle size is about 15 nanometers.
19. (amended) The method according to claim 1 wherein the method includes a further step prior to step (d), the further step comprising mixing a polymer component into the gel, the polymer component being capable of bonding with the gel and particulate material during step (d).
20. The method according to claim 19 wherein the polymer material is either hydrophobic or rendered hydrophobic during step (d).
21. (amended) The method according to claim 1 wherein the method includes a further step prior to step (d), the further step comprising adding a surface modifier to the gel, the surface modifier being capable of increasing the intrinsic chemical hydrophobicity of a hydrophobic surface formed with the modified gel.
22. The method according to claim 21 wherein the surface modifier further enhances bonding between the particulate material and the gel.
23. (amended) The method according to claim 21 wherein the surface modifier is a compound including one or more hydrophobic groups and one or more condensation cure groups.
24. (amended) The method according to claim 23 wherein the one or more hydrophobic groups include one or more of the following groups: methyl; ethyl; vinyl; and trifluoropropyl.

25. (amended) The method according to claim 23 wherein the one or more condensation cure groups include one or more of the following groups: acetoxo; enoxo; oxime; alkoxy; and amine.

26. (amended) The method according to claim 1 wherein the particulate material comprises a flame-hydrolyzed silica powder, and the gel comprises a silicon dioxide gel

27. (amended) The method according to claim 19 wherein the polymer component comprises polydimethylsiloxane (PDMS) .

28. (amended) A method of forming a coating on a substrate, comprising the steps of:

- forming a modified gel in accordance with the method of claim 1;
- applying the modified gel to the substrate; and
- treating the applied modified gel such that a coating is formed on the substrate, the coating having a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water forms a contact angle of at least 150°.

29. The method according to claim 28 wherein the hydrophobic surface of the coating is such that water forms a contact angle on it of at least 155°.

30. The method according to claim 28 wherein the hydrophobic surface is such that water forms a contact angle on it of at least 160°.

31. The method according to claim 28 wherein the hydrophobic surface is such that water forms a contact angle on it of at least 165°.

32. (amended) The method according to claim 1 wherein the modified gel is in the form of a slurry.

33. (amended) The method according to claim 28 wherein the step of applying the modified gel to the substrate comprises using one of the following techniques: spin coating; dip coating; or spray coating.
34. (amended) The method according to claim 28 wherein the step of treating the mixture comprises drying the applied modified gel such that a solid coating is formed.
35. The method according to claim 34 wherein the step of drying includes a step of heating the applied modified gel to a temperature which is sufficient to evaporate any solvents.
36. (amended) The method according to claim 34 wherein the step of drying the coating comprises heating the coating to a temperature in the range from 120° to 400°C.
37. (amended) A modified gel produced by a method in accordance with claim 1.
38. (amended) An object having a surface, at least a portion of which is coated with a hydrophobic coating formed from a modified gel made by a method in accordance with claim 1.
39. (amended) A hydrophobic coating produced by a method in accordance with claim 28.
40. (amended) An object having a surface, at least a portion of which is coated with a hydrophobic coating produced by a method in accordance with claims 28.

JC10 Rec'd PCT/PTO 20 FEB 2002

ATTACHMENT B

Marked Up Replacement Claims

Following herewith is a marked up copy of each rewritten claim together with all other pending claims.

Following herewith is a marked up copy of each rewritten claim.

1. A method of forming a material capable of being applied to a surface, the method including the steps of:
 - (a) providing precursors capable of reacting to form a gel,
 - (b) reacting the precursors together to form the gel;
 - (c) adding a particulate material to the gel to form a mixture, the particulate material being capable of chemically bonding with the gel; and
 - (d) treating the mixture such that a modified gel is formed in which the particulate material is bound to the gel, and the modified gel is capable of forming a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water has a contact angle on the surface of at least 150°.
2. The method according to claim 1 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 155°.
3. (amended) The method according to ~~either claim 1 or claim 2~~ wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 160°.
4. (amended) The method according to ~~any one of the preceding claims~~ 1 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 165°.

5. (amended) The method according to ~~any one of the preceding claims~~ 1 wherein the precursors provided in step (a) include at least water, a solvent, and a metal alkoxide.
6. The method according to claim 5 wherein the solvent comprises an alcohol.
7. The method according to claim 6 wherein the alcohol is selected from the following group: methanol; ethanol; isopropanol; and butanol.
8. The method according to claim 5 wherein the solvent is selected from a group comprising: hexane; and diethyl ether.
9. (amended) The method according to ~~any one of claims 5-8~~ wherein the metal alkoxide is selected from the following group: tetramethoxysilane; tetraethoxysilane; titanium tetraisopropoxide; titanium tetrameahoxide; titanium tetraethoxide; titanium tetrabutoxide; and zirconium n-butoxide.
10. (amended) The method according to ~~any one of the preceding claims~~ 1 wherein step (b) of reacting the precursors together comprises refluxing the precursors for an extended period.
11. (amended) The method according to ~~any one of the preceding claims~~ 1 wherein the particulate material comprises particles having substantially equal diameters.
12. (amended) The method according to ~~any one of claims 1-10~~ wherein the particulate material comprises particles having a spectrum of diameters.
13. (amended) The method according to ~~either claim 11 or claim 12~~ wherein at least some of the particles have diameters within a range from 1 nanometer to 1 micrometer.

14. (amended) The method according to ~~either claim 11 or claim 12~~ wherein at least some of the particles have diameters within a range from 1 nanometer to 100 nanometers.
15. The method according to claim 11 wherein substantially all particles have diameters within a range from 1 nanometer to 500 micrometers.
16. (amended) The method according to ~~either claim 11 or claim 12~~ wherein the particles have a primary particle diameter in a range from 5 nanometers to 50 nanometers.
17. (amended) The method according to ~~either claim 11 or claim 12~~ wherein the particles have an average particle size in a range from 5 nanometers to 20 nanometers.
18. (amended) The method according to ~~either claim 11 or claim 12~~ wherein the average particle size is about 15 nanometers.
19. (amended) The method according to ~~any one of the preceding claims 1~~ wherein the method includes a further step prior to step (d), the further step comprising mixing a polymer component into the gel, the polymer component being capable of bonding with the gel and particulate material during step (d).
20. The method according to claim 19 wherein the polymer material is either hydrophobic or rendered hydrophobic during step (d).
21. (amended) The method according to ~~any one of the preceding claims 1~~ wherein the method includes a further step prior to step (d), the further step comprising adding a surface modifier to the gel, the surface modifier being capable of increasing the intrinsic chemical hydrophobicity of a hydrophobic surface formed with the modified gel.

22. The method according to claim 21 wherein the surface modifier further enhances bonding between the particulate material and the gel.

23. (amended) The method according to ~~either claim 21 or claim 22~~ wherein the surface modifier is a compound including one or more hydrophobic groups and one or more condensation cure groups.

24. (amended) The method according to claim 23 wherein the one or more hydrophobic groups include one or more of the following groups: methyl; ethyl; vinyl; and trifluoropropyl.

25. (amended) The method according to ~~either claim 23 or claim 24~~ wherein the one or more condensation cure groups include one or more of the following groups: acetoxy; enoxy; oxime; alkoxy; and amine.

26. (amended) The method according to ~~any one of the preceding claims 1~~ wherein the particulate material comprises a flame-hydrolysed hydrolyzed silica powder, and the gel comprises a silicon dioxide gel

27. (amended) The method according to ~~any one of the preceding claims in combination with claim 19~~ wherein the polymer component comprises polydimethylsiloxane (PDMS)

28. (amended) A method of forming a coating on a substrate, comprising the steps of:

- forming a modified gel in accordance with the method of ~~any one of the preceding claims 1~~;
- applying the modified gel to the substrate; and
- treating the applied modified gel such that a coating is formed on the substrate, the coating having a surface which is chemically hydrophobic and has a surface

roughness which physically enhances the surface hydrophobicity, such that water forms a contact angle of at least 150°.

29. The method according to claim 28 wherein the hydrophobic surface of the coating is such that water forms a contact angle on it of at least 155°.

30. The method according to claim 28 wherein the hydrophobic surface is such that water forms a contact angle on it of at least 160°.

31. The method according to claim 28 wherein the hydrophobic surface is such that water forms a contact angle on it of at least 165°.

32. (amended) The method according to ~~any one of claims 1-31~~ wherein the modified gel is in the form of a slurry.

33. (amended) The method according to ~~any one of claims 28-32~~ wherein the step of applying the modified gel to the substrate comprises using one of the following techniques: spin coating; dip coating; or spray coating.

34. (amended) The method according to ~~any one of claims 28-33~~ wherein the step of treating the mixture comprises drying the applied modified gel such that a solid coating is formed.

35. The method according to claim 34 wherein the step of drying includes a step of heating the applied modified gel to a temperature which is sufficient to evaporate any solvents.

36. (amended) The method according to ~~either claim 34 or claim 35~~ wherein the step of drying the coating comprises heating the coating to a temperature in the range from 120° to 400°C.

37. (amended) A modified gel produced by a method in accordance with ~~any one of~~ claims 1-27.

38. (amended) An object having a surface, at least a portion of which is coated with a hydrophobic coating formed from a modified gel made by a method in accordance with ~~any one of~~ claim 1-27.

39. (amended) A hydrophobic coating produced by a method in accordance with ~~any one of~~ claims 28-36.

40. (amended) An object having a surface, at least a portion of which is coated with a hydrophobic coating produced by a method in accordance with ~~any one of~~ claims 28-36.

HYDROPHOBIC MATERIAL**Technical Field**

The invention relates to the technology of coatings. In particular, the invention relates to coating materials which are hydrophobic, and to methods for making coatings from those materials.

Background Art

Hydrophobic coatings are water-proof coatings which have immediate uses in reducing icing and fouling of other surface. Such coatings can also render protected surfaces resistant to attachment by water soluble electrolytes such as acids and alkalies, and by microorganisms.

In the past, surfaces have been protected against encrustation, corrosion, icing and fouling by means of coatings containing polymer films, hydrophobic solid fillers and hydrophobic liquids. One disadvantage of the use of such coatings is that they do not achieve multi-purpose protection since they are not generally versatile enough to protect against damage from a variety of causes.

It is well understood that the wettability of various materials is dependent on both the physical and chemical heterogeneity of the material. The notion of using the contact angle θ made by a droplet of liquid on a surface of a solid substrate as a quantitative measure of the wetting ability of the particular solid has also long been well understood. If the liquid spreads completely across the surface and forms a film, the contact angle θ is 0° . If there is any degree of beading of the liquid on the surface of the substrate, the surface is considered to be non-wetting. For water, the substrate surface is usually considered to be hydrophobic if the contact angle is greater than 90° .

- 2 -

Examples of materials on which liquid droplets have high contact angles include water on paraffin, in which there is a contact angle of about 107° . Many applications require a hydrophobic coating with a high contact angle of at least 150° , and preferably at least 165° .

A "gel" is a substance that contains a continuous solid skeleton enclosing a continuous liquid phase. The liquid prevents the solid from collapsing, and the solid prevents the liquid from escaping. The solid skeleton can be formed by linking colloidal particles together.

The present inventors have now developed methods for producing materials which, when coated on a surface, render that surface hydrophobic.

Summary of the Invention

In a first aspect, the present invention provides a method of forming a material capable of being applied to a surface, the method including the steps of:

- (a) providing precursors capable of reacting to form a gel;
- (b) reacting the precursors together to form the gel;
- (c) adding a particulate material to the gel to form a mixture, the particulate material being capable of chemically bonding with the gel; and
- (d) treating the mixture such that a modified gel is formed in which the particulate material is bound to the gel, and the modified gel is capable of forming a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water has a contact angle on the surface of at least 150° .

In a second aspect, the present invention provides a method of forming a coating on a substrate, the method

- 3 -

including steps (a) to (d) of the first aspect of the present invention, and further including the steps of:

(e) applying the modified gel to the substrate; and

(f) treating the applied modified gel such that a coating is formed on the substrate, the coating having a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water forms a contact angle of at least 150°.

Preferably, the hydrophobic surface defined in either the first or the second aspect of the present invention is such that water forms a contact angle of at least 155° on it. More preferably, the contact angle is at least 160°. Even more preferably, the contact angle is at least 165°.

The hydrophobicity of the hydrophobic material when applied to a surface is preferably due to both the chemical properties of the modified gel and physical roughness of the material. It is envisaged that the modified gel of the first aspect of the present invention could be used to make solid materials in a range of possible forms, including bulk materials, thick coatings, and thin films.

The gel functions as a cross-linking agent which binds the particulate material, and attaches the modified gel to the substrate if required. Any known process for forming a gel may be used. Typically, the precursors defined in step (a) of the first and second aspects of the present invention at least include water, a solvent, and a metal alkoxide such as one of the following:

- tetramethoxysilane (abbreviated TMOS), $\text{Si}(\text{OCH}_3)_4$
- tetraethoxysilane (abbreviated TEOS), $\text{Si}(\text{OCH}_2\text{CH}_3)_4$;
- titanium tetraisopropoxide, $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_4$;
- titanium tetramethoxide, $\text{Ti}(\text{OCH}_3)_4$;

- 3a -

- titanium tetraethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$;
- titanium tetrabutoxide, $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$;
- zirconium n-butoxide, $\text{Zr}(\text{O}-n-\text{C}_4\text{H}_9)_4$.

30 Step (d) of the first and second aspects of the invention may be implemented by firstly thoroughly mixing the mixture, such as in an ultrasonic bath. Optionally, an alcohol such as isopropanol may be added to the mixture

- 5 -

during this step to aid in dispersing the particulate material. Secondly, the mixture may be refluxed to cause chemical bonding between the particulate material and the gel.

5 Step (e) of applying the modified gel to a substrate may be carried out by any known technique of forming a coating from a liquid, such as spin coating, dip coating or spray coating.

10 Step (f) may involve drying the applied modified gel until a solid coating is formed. There may be solvents which need to be removed from the modified gel, and in such a case, the drying may include heating the applied modified gel to a temperature which is at least high enough to evaporate the solvents. It will be appreciated
15 that the drying temperature will depend on the melting point of the substrate and the type of gel. The drying time for a particular application will usually depend on the temperature used, and to some extent on the thickness of the coating. In the case of silica coatings, it has
20 been found that a heating temperature of in the range from 120°C to 400°C over a period of 10-30 minutes is suitable when the substrate is capable of withstanding such a temperature. Vacuum drying, or a combination of vacuum drying and heating, may be preferable when the substrate
25 has a low melting point.

 Elasticity and flexibility of the coating may be enhanced by adding a polymer component to the gel during step (c). Alternatively, the polymer component may be added to the gel either directly before or directly after
30 step (c). The polymer component preferably bonds with the gel and particulate material during step (d), and is preferably either hydrophobic, or rendered hydrophobic by the reaction in step (d).

In a preferred embodiment, the particulate material consists of flame-hydrolysed silica powder, and the gel precursors include a compound capable of forming a silicon dioxide gel, such as either TMOS or TEOS. A suitable polymer component in this case is polydimethylsiloxane (PDMS), a polymer with hydroxyl groups terminating the ends of each chain. The resultant modified gel consists of silica particles chemically bound to a siloxane network, and surrounded by liquid.

- 7 -

Flame-hydrolysed silica powder is relatively inexpensive and commercially available as AerosilTM silica powder from Degussa Limited with particles having a primary size in the range of 5-50 nm. Although flame-
5 hydrolysed silica particles are initially hydrophilic, the surface chemistry is changed during step (d) by converting silanol functional groups (=Si-OH) on the surfaces of the particles, to siloxane bonds (=Si-O-Si=). This interaction has the advantage of rendering the particles hydrophobic
10 through reaction with the PDMS or a surface modifier. A modified gel made in this way is particularly hydrophobic for two reasons. Firstly, the chemical properties of siloxane bonds make it inherently hydrophobic. Secondly, the small size of the particles in the flame-hydrolysed
15 silica gives the modified gel a small-scale roughness which increases the hydrophobicity of the silicon dioxide.

Although silica and silica-based particles are preferred, other materials of hydrophobic character which can be prepared with a sufficiently small particle size
20 could be used in conjunction with a hydrophobic gel capable of bonding to the particles. Examples include particles and gels formed from a metal oxide, such as titanium dioxide. For instance, titanium dioxide particles could be reacted with a titanium dioxide gel formed from
25 titanium tetraisopropoxide.

A specific embodiment of the first and second aspects of the invention will now be described. In step (a) the precursors are 5 g of TEOS, 1.7 g of water acidified with HCl to a pH of approximately 4, and 2.7 g of ethanol. In
30 step (b) the mixture is refluxed for 6-36 hours to form a silica gel. In step (c) the particulate material added to the gel is 0.5 g to 2.5 g of flame-hydrolysed silica powder, forming a mixture. About 0.5 g to 5 g of PDMS and

- 8 -

approximately 50 g of isopropanol is then added to the mixture. In step (d), the reactants are mixed well and vibrated in an ultrasonic bath for 15 to 30 minutes, forming a uniform slurry. The slurry is then allowed to
5 reflux for another 6-24 hours to make the silica gel chemically bond with the silica powder and PDMS. The slurry is the modified gel which can be used to form a coating according to the second aspect of the present invention. In a preferred embodiment, step (e) includes
10 depositing drops of the slurry onto a substrate while the substrate is spinning. Typical substrates are metals, glasses, and ceramics. The substrate is spun at spin rate of 1000 to 2000 rpm. In step (f) the coated substrate is placed in an oven at a temperature of about 400°C for 10
15 to 30 minutes.

In a third aspect, the present invention provides a modified gel produced by the method according to the first aspect of the present invention.

In a fourth aspect, the present invention provides an
20 object having a surface, at least a portion of which is coated with a hydrophobic coating formed from a modified gel made by the method according to the first aspect of the present invention.

In a fifth aspect, the present invention provides a
25 hydrophobic coating produced by the method according to the second aspect of the present invention.

In a sixth aspect, the present invention provides an object having a surface, at least a portion of which is coated with a hydrophobic coating produced by the method
30 according to the second aspect of the present invention.

In a seventh aspect, the present invention provides a use of the method according to the second aspect of the

present invention to coat at least a portion of a surface of an object.

Surfaces which can be treated with the hydrophobic coating include metals, alloys, glasses, ceramics, composites, but can also include other materials. The surface treatment can be used to inhibit corrosion or the formation of crystallisation centres. The treatment can be used to prevent icing on surfaces, to produce anti-gripping hydrophobic coatings for aboveground fixed facilities such as buildings and other structures, to provide anti-icing and anti-corrosion coatings for aircraft, or to provide anti-icing, anti-fouling and anti-corrosion coatings for maritime and inland waterway vessels. A hydrophobic anti-fouling coating formed from silica has the advantage that it much less toxic to the marine environment than most currently-available coatings.

Other uses include increasing the resistance of roofs to microflora colonisation. The hydrophobic coatings may also be used for extending the survivability, performance, and reliability of instruments and equipment.

Still other uses envisaged for the hydrophobic coatings include reducing drag in vessels such as canoes, yachts, ships, and other watercraft, improving the corrosion resistance of cooling systems in internal combustion engines utilising closed heat exchangers having liquid heat transfer agents, providing anti-corrosive and anti-icing coatings for undercarriages of vehicles such as tractors and combines and for agricultural machinery in general.

The hydrophobic coating according to the present invention may also be used to waterproof building foundations and structures and radioactive waste storage facilities, extend the operating service life of water

- 10 -

cooling towers, protect railroad ties from microflora, provide anti-icing coatings for cooling chambers, refrigerators and chillers, extend the life cycle of hydroelectric power dams, and improve the efficiency of wind-driven motors. Metal parts coated in the hydrophobic coating would be less prone to rust because water would be repelled from the metal surface. The hydrophobic coating could also be used on windows, such as car windscreens, if the coating is largely transparent to visible light.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

In order that the present invention may be more clearly understood, embodiments will be described with reference to the following examples and the accompanying drawings.

Brief Description of Drawings

Figure 1 is an image produced by a scanning electron microscope at a magnification of 5,000 for a silica hydrophobic coating; and

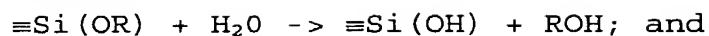
Figure 2 is higher magnification scanning electron microscope image (x100,000) for the same hydrophobic coating shown in Figure 1.

Modes for Carrying Out the Invention

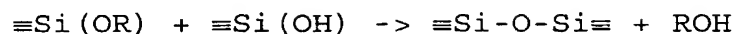
A method of making a silica-based hydrophobic coating will now be described. The two fundamental chemical reactions of the sol-gel process in this case are:

- 11 -

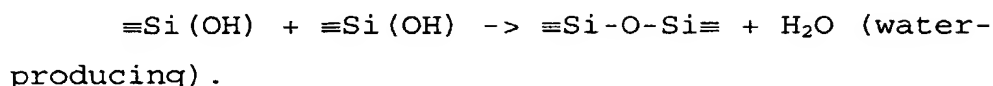
(1) hydrolysis,



(2) condensation,



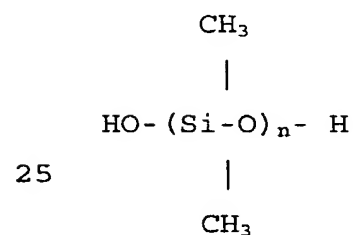
5 (alcohol-producing), and



The hydrolysis and condensation reactions are usually concurrent.

10 The precursor used for preparing the gel is tetraethoxysilane ($\text{Si}(\text{OCH}_2\text{CH}_3)_4$), and the particulate material is flame-hydrolysed silica powder (^{Aerosil™} silica). The silica powder has a primary particle size of 5 to 50 nm, and the specific surface of the powder is
15 about 50-600 m² /g. The large specific surface is an important characteristic of the silica since it influences the surface roughness of a coating, and is thereby linked to the hydrophobicity of the coating.

The polymer component is polydimethylsiloxane
20 (PDMS):



PDMS is a polymer which is unusually resistant to heat, being able to withstand temperatures up to about
30 400°C without deformation. It also has high electrical resistance, and is able to withstand outdoor exposure to UV radiation with little or no deformation or degradation for at least 10 years. PDMS is terminated with hydroxyl

- 13 -

2.7 g of ethanol. Reflux the mixture for about 6-36 hours to form the silica gel.

- Add to the mixture:

0.5 to 5 g of PDMS with viscosity of 90-150 cSt;

5 0.5 to 2.5 g of Aerosil™ 200 (flame-hydrolysed silica powder with an average individual particle of size 15 nm) obtained from Degussa Limited; and approximately 50 g of isopropanol.

- Mix the reactants well and vibrate in an ultrasonic bath
10 for 15 to 30 minutes to disperse the particles and form a uniform slurry. Typical vibration frequencies of about 40 kHz are sufficient.
- Remove the reactants from the ultrasonic bath, and
15 reflux for about 6 hours. The resultant slurry is now suitable for preparing hydrophobic coatings.
- Deposit drops of the slurry onto a substrate using spin
20 coating. A spin rate of 1000 to 2000 rpm has been found to be sufficient, but will depend on the viscosity of the slurry, the coating thickness required, and the surface of the substrate. A range of substrate types can be used, including metals, glasses, silicon, ceramics, polymers, and composites. However, the substrate should be reasonably flat.
- Place the coated substrate in an oven at a temperature
25 of about 400°C for 10 to 30 minutes.

Figures 1 and 2 show scanning electron microscope images of the surface of a hydrophobic coating produced using the above technique. The surface is viewed at a
30 magnification of 5,000 (Figure 1) and 100,000 (Figure 2). It is clear from the images that the coating has an extremely rough surface. Moreover, the dimensions of the

- 14 -

surface roughness span at least three orders of magnitude, ranging from tens of nanometres to tens of microns.

Example 2

5 In this comparative example, example 1 was repeated except that the amount of Aerosil 200 was changed to 1.5g. With the higher PDMS/Aerosil ratio, there should be more bonding between silica particles without decreasing the hydrophobicity.

10

Example 3

 In this comparative example, example 1 was repeated except that the amount of TEOS was reduced from 5g to 2.5g. It was found that with less TEOS acting as a cross-
15 linking agent, the hydrophobicity of the coating does not decrease. With a comparatively higher PDMS content in this coating, the flexibility of the coating might increase. However, the durability of the coating might decrease due to less bonding between silica particles, and between
20 particles and the substrate.

Example 4

 In this comparative example, example 2 was repeated except that the amount of TEOS was reduced from 5g to
25 2.5g. It was found that with this moderate TEOS/Aerosil ratio and PDMS/Aerosil ratio, the final coating possesses good durability and flexibility.

Example 5

 In this comparative example, example 1 was repeated
30 except that the viscosity of PDMS used was increased from 90-150 cSt to 2,000 cSt. With longer PDMS chains in the coating, the flexibility of the coating might increase.

Example 6

In this comparative example, example 2 was repeated except that the viscosity of PDMS used was increased from 90-150 cSt to 2,000 cSt.

5

Example 7

In this comparative example, example 3 was repeated except that the viscosity of PDMS used was increased from 90-150 cSt to 2,000 cSt.

10

Example 8

In this comparative example, example 4 was repeated except that the viscosity of PDMS used was increased from 90-150 cSt to 2,000 cSt.

15

Example 9

In this comparative example, example 1 was repeated except that the viscosity of PDMS used was increased from 90-150 cSt to 20,000 cSt or higher. With even longer PDMS chains in the coating, the flexibility of the coating might increase further.

20

Example 10

In this comparative example, example 2 was repeated except that the viscosity of PDMS used was increased to 20,000 cSt.

25

Example 11

In this comparative example, example 3 was repeated except that the viscosity of PDMS used was increased to 20,000 cSt.

30

- 16 -

Example 12

In this comparative example, example 4 was repeated except that the viscosity of PDMS used was increased to 20,000 cSt.

5.

Example 13

In this comparative example, example 1 was repeated except that Aerosil 200 was replaced by Aerosil 8202 (average individual particle size of 17 nm), which was also obtained from Degussa Limited. It was found that with these particles the hydrophobicity of the resultant coating does not decrease substantially.

10

Example 14

In this comparative example, example 1 was repeated except that the Aerosil 200 was replaced by tin oxide powder with an average particle size of about 300-500 nm. It was found that with the significant increase in particle size, the hydrophobicity of the coating decreased, but not substantially. This may suggest that hydrophobicity is influenced by surface roughness, and to a lesser extent by particle size.

15

20

Example 15

In this comparative example, example 1 was repeated except that the Aerosil 200 was replaced by antimony(III) oxide powder with an average particle size of around 5,000 nm. It was found that this significant increase in particle size substantially decreased the hydrophobicity of the coating.

25

30

Table 1 below shows the results of contact angle measurements made on coatings produced in examples 1-14.

	Example No.	Contact Angle (degrees)
30	1	167
	2	164
	3	167
	4	153

- 18 -

	5	158
	6	174
	7	169
	8	145
5	9	164
	10	158
	11	172
	12	170
	13	159
10	14	151
	15	115
	16	155

Table 1.

15 It will be appreciated by persons skilled in the art
that numerous variations and/or modifications may be made
to the invention as shown in the specific embodiments
without departing from the spirit or scope of the
invention as broadly described. The present embodiments
20 are, therefore, to be considered in all respects as
illustrative and not restrictive.

- 19 -

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of forming a material capable of being applied to a surface, the method including the steps of:
 - 5 (a) providing precursors capable of reacting to form a gel;
 - (b) reacting the precursors together to form the gel;
 - (c) adding a particulate material to the gel to form a mixture, the particulate material being capable of chemically bonding with the gel; and
 - 10 (d) treating the mixture such that a modified gel is formed in which the particulate material is bound to the gel, and the modified gel is capable of forming a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water has a contact angle on the surface of at least 150°.
2. The method according to claim 1 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 155°.
- 20 3. The method according to either claim 1 or claim 2 wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 160°.
- 25 4. The method according to any one of the preceding claims wherein the modified gel is capable of forming a hydrophobic surface on which water has a contact angle of at least 165°.
5. The method according to any one of the preceding claims wherein the precursors provided in step (a) include at least water, a solvent, and a metal alkoxide.
- 30 6. The method according to claim 5 wherein the solvent

- 20 -

comprises an alcohol.

7. The method according to claim 6 wherein the alcohol is selected from the following group:
methanol;
5 ethanol;
isopropanol;
and butanol.
8. The method according to claim 5 wherein the solvent is selected from a group comprising: hexane; and
10 diethyl ether.
9. The method according to any one of claims 5-8 wherein the metal alkoxide is selected from the following group:
tetramethoxysilane;
15 tetraethoxysilane;
titanium tetraisopropoxide;
titanium tetramethoxide;
titanium tetraethoxide;
titanium tetrabutoxide;
20 zirconium n-butoxide.
10. The method according to any one of the preceding claims wherein step (b) of reacting the precursors together comprises refluxing the precursors for an extended period.
- 25 11. The method according to any one of the preceding claims wherein the particulate material comprises particles having substantially equal diameters.
12. The method according to any one of claims 1-10 wherein the particulate material comprises particles
30 having a spectrum of diameters.
13. The method according to either claim 11 or claim 12 wherein at least some of the particles have diameters within a range from 1 nanometer to 1 micrometer.

- 21 -

14. The method according to either claim 11 or claim 12 wherein at least some of the particles have diameters within a range from 1 nanometer to 100 nanometers.
15. The method according to claim 11 wherein
5 substantially all particles have diameters within a range from 1 nanometer to 500 micrometers.
16. The method according to either claim 11 or claim 12 wherein the particles have a primary particle diameter in a range from 5 nanometers to 50
10 nanometers.
17. The method according to either claim 11 or claim 12 wherein the particles have an average particle size in a range from 5 nanometers to 20 nanometers.
18. The method according to either claim 11 or claim 12
15 wherein the average particle size is about 15 nanometers.
19. The method according to any one of the preceding claims wherein the method includes a further step prior to step (d), the step comprising mixing a
20 polymer component into the gel, the polymer component being capable of bonding with the gel and particulate material during step (d).
20. The method according to claim 19 wherein the polymer material is either hydrophobic or rendered
25 hydrophobic during step (d).
21. The method according to any one of the preceding claims wherein the method includes a further step prior to step (d), the further step comprising adding a surface modifier to the gel, the surface modifier
30 being capable of increasing the intrinsic chemical hydrophobicity of a hydrophobic surface formed with the modified gel.
22. The method according to claim 21 wherein the surface

- 22 -

modifier further enhances bonding between the particulate material and the gel.

23. The method according to either claim 21 or claim 22 wherein the surface modifier is a compound including one or more hydrophobic groups and one or more condensation cure groups.

24. The method according to claim 23 wherein the one or more hydrophobic groups include one or more of the following groups:

methyl;
ethyl;
vinyl;
trifluoropropyl.

25. The method according to either claim 23 or claim 24 wherein the one or more condensation cure groups include one or more of the following groups:

acetoxo;
enoxo;
oxime;
alkoxo;
amine.

26. The method according to any one of the preceding claims wherein the particulate material comprises a flame-hydrolysed silica powder, and the gel comprises a silicon dioxide gel.

27. The method according to any one of the preceding claims in combination with claim 19 wherein the polymer component comprises polydimethylsiloxane (PDMS).

28. A method of forming a coating on a substrate, comprising the steps of:

- forming a modified gel in accordance with the method of any one of the preceding claims;

- 23 -

- applying the modified gel to the substrate; and
 - treating the applied modified gel such that a coating is formed on the substrate, the coating having a surface which is chemically hydrophobic and has a surface roughness which physically enhances the surface hydrophobicity, such that water forms a contact angle of at least 150°.
- 5
29. The method according to claim 28 wherein the hydrophobic surface of the coating is such that water forms a contact angle on it of at least 155°.
- 10
30. The method according to claim 28 wherein the hydrophobic surface is such that water forms a contact angle on it of at least 160°.
31. The method according to claim 28 wherein the hydrophobic surface is such that water forms a contact angle on it of at least 165°.
- 15
32. The method according to any one of claims 1-31 wherein the modified gel is in the form of a slurry.
33. The method according to any one of claims 28-32 wherein the step of applying the modified gel to the substrate comprises using one of the following techniques:
- 20
- spin coating;
 - dip coating; or
 - spray coating.
- 25
34. The method according to any one of claims 28-33 wherein the step of treating the mixture comprises drying the applied modified gel such that a solid coating is formed.
- 30
35. The method according to claim 34 wherein the step of drying includes a step of heating the applied modified gel to a temperature which is sufficient to evaporate any solvents.

- 24 -

36. The method according to either claim 34 or claim 35 wherein the step of drying the coating comprises heating the coating to a temperature in the range from 120° to 400°C.
- 5 37. A modified gel produced by a method in accordance with any one of claims 1-27.
38. An object having a surface, at least a portion of which is coated with a hydrophobic coating formed from a modified gel made by a method in accordance with any one of claim 1-27.
- 10 39. A hydrophobic coating produced by a method in accordance with any one of claims 28-36.
40. An object having a surface, at least a portion of which is coated with a hydrophobic coating produced by a method in accordance with any one of claims 28-36.
- 15 41. A method of forming a material capable of being applied to surface, substantially as herein described with reference to the accompanying examples and Figures.
- 20 42. A method of forming a coating on a substrate substantially as herein described with reference to the accompanying examples and Figures.
- 25

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(54) Title: HYDROPHOBIC MATERIAL

(57) Abstract: The present invention provides a method of forming a modified gel capable of forming a hydrophobic surface on which water has a contact angle of at least 150°. The invention also provides a method of forming a hydrophobic coating from the modified gel. In some embodiments, the hydrophobic coating has an extremely high hydrophobicity with a contact angle in excess of 165°, and good substrate adhesion. The method involves bonding a gel with particulate matter. It is believed that the chemical hydrophobicity of the gel is enhanced by the physical roughness of the particulate matter.

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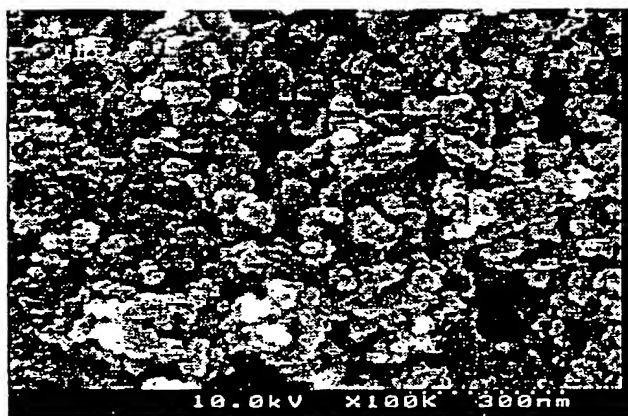


FIGURE 1

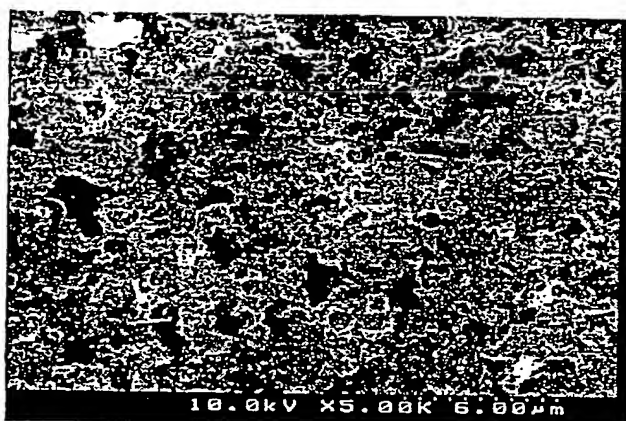


FIGURE 2

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	Serial No.	10/
Declaration Submitted with Initial Filing	Filing Date	February 20, 2002
<input checked="" type="checkbox"/> Declaration Submitted after Initial Filing		

As a below named inventor, I hereby declare that:
My residence, mailing address and citizenship are as stated below next to my name.
I believe I am the original and first inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled.
HYDROPHOBIC MATERIAL
the specification of which:
is attached hereto
OR
☒ was filed on 21 August 2000 as PCT International Application No. PCT/AU00/00993,
and (if applicable) was amended on .
I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment specifically referred to above.
I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.
I hereby claim FOREIGN PRIORITY benefits under 35 USC 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's certificate(s), or 365(a) of any PCT international application which designated at least one country other than the US, listed below and have also identified below by checking the box, any foreign application for patent, inventor's certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed. (ADDITIONAL APPLICATIONS IDENTIFIED ON ADDITIONAL INFORMATION SHEET)

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As a named inventor, I hereby appoint the registered practitioners of **LARSON & TAYLOR, PLC** associated with Customer Number 000881 to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. Direct all correspondence to that Customer Number.
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at TEL (703) 739-4900 (Fax: 703-739-9577) e-mail: bschulman@larsontaylor.com
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 USC 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon. (ADDITIONAL INVENTORS IDENTIFIED ON ADDITIONAL INFORMATION SHEET)

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